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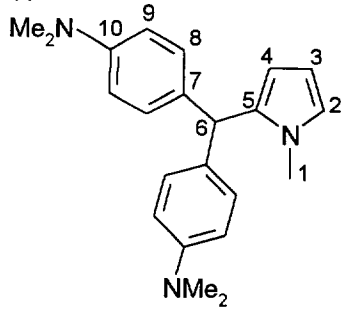
Supporting Information

I. Preparative work. All reactions have been performed according to the general procedure described in the experimental section using the quantities given in Table 1. All assignments of the NMR resonances have been based on DEPT, HETCOR, H,H-COSY and COLOCS-experiments.

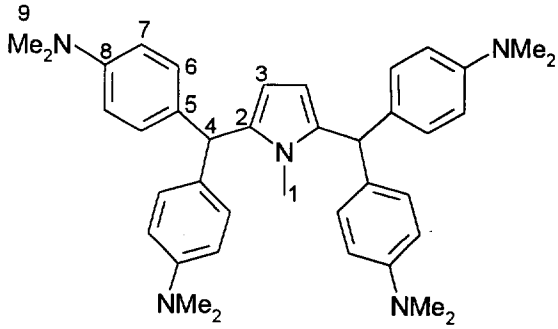
- Reaction of $2a^+BF_4^-$/$2a^+OTf^-$ with 1a. Temperature: 20 °C. Separation and purification of the products by column chromatography (hexane/ethyl acetate = 3/1 (v/v)).

2-[Bis(4-(*N*, *N*-dimethylamino)phenyl)methyl]-*N*-methylpyrrole (3a).



^{1}H NMR: δ = 6.98-6.94 (AA'BB'-system, J_{AB}= 8.7 Hz, 4 H, 8-H), 6.67-6.63 (AA'BB'-system, J_{AB}= 8.7 Hz, 4 H, 9-H), 6.57 - 6.55 (m, 1 H, 2-H), 6.02-6.00 (m, 1 H, 3-H), 5.53-5.51 (m, 1 H, 4-H), 5.20 (br. s, 1 H, 6-H), 3.32 (s, 3 H, 1-H), 2.90 (s, 12 H, 11-H); ^{13}C NMR: δ = 149.0 (s, C-10), 136.4 (s, C-5), 131.6 (s, C-7), 129.4 (d, C-8), 121.6 (d, C-2), 112.5 (d, C-9), 108.8 (d, C-4), 106.0 (d, C-3),47.5 (d, C-6), 40.7 (q, C-11), 33.9 (q, C-1). Recrystallization from pentane yields colorless crystals, mp 209-211 °C. Anal. Calcd. for $C_{22}H_{27}N_3$ (333.5): C, 79.24; H, 8.16; N, 12.60. Found: C, 78.97; H, 8.08; N, 12.42.

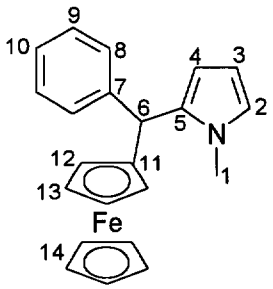
2,5-Bis[bis(4-(*N*, *N*-dimethylamino)phenyl)methyl]-*N*-methylpyrrole (4a).



^{1}H NMR: δ = 6.98-6.95 (AA'BB'-system, J_{AB}= 8.7 Hz, 8 H, 6-H), 6.65-6.62 (AA'BB'-system, J_{AB}= 8.7 Hz, 8 H, 7-H), 5.39 (s, 2 H, 3-H), 5.16 (s, 2 H, 4-H), 2.99 (s, 3 H, 1-H), 2.89 (s, 24 H, 9-H); ^{13}C NMR: δ = 149.0 (s, C-8), 136.3 (s, C-2), 132.0 (s, C-5), 129.5 (d, C-6), 112.5 (d, C-7), 107.2 (d, C-3), 48.0 (d, C-4), 40.7 (q, C-9), 30.9 (q, C-1).

-Reaction of 2b-OAc with 1a. Temperature: 0 °C. Separation and purification of the products by column chromatography (hexane/ethyl acetate = 5/1 (v/v) or = 20/1 (v/v)).

2-(Ferrocenyl-phenyl-methyl)- *N*-methylpyrrole (3b).



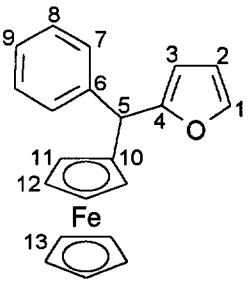
^{1}H NMR: δ = 7.36-7.15 (m, 5 H, 8-H, 9-H, and 10-H), 6.48-6.45 (m, 1 H, 2-H), 5.99-5.97 (m, 1 H, 3-H), 5.70-5.68 (m, 1 H, 4-H), 5.02 (br. s, 1 H, 6-H), 4.20-3.79 (4 × m, 4 H, 12-H and 13-H), 4.00 (s, 5 H, 14-H), 3.25 (s, 3 H, 1-H); ^{13}C NMR: δ = 142.2 (s, C-7), 136.2 (s, C-5), 128.9 (d, C-9), 128.1 (d, C-8), 126.4 (d, C-10), 121.6 (d, C-2), 108.0 (d, C-4), 106.0 (d, C-3), 91.4 (s, C-11), 68.6 (d, C-14), 68.5-67.1 (d, C-12, C-13), 44.3 (d, C-6), 34.0 (q, C-1).

Orange crystals, mp = 91 - 93 °C. Anal. Calcd. for $C_{22}H_{21}NFe$ (355.3): C, 74.38; H, 5.96; N, 3.94. Found: C, 74.24; H, 5.87; N, 3.94.

Approximately 10 % of **4b** could be seen in the ^{1}H NMR spectrum of the raw product but all attempts to separate and purify **4b** failed.

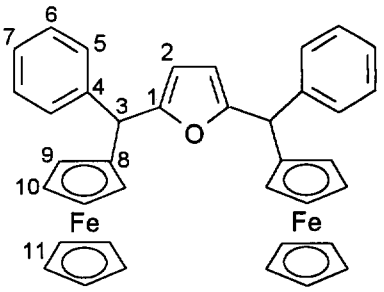
-Reaction of 2b-OAc with 1b. Temperature: ambient. Separation and purification of the products by column chromatography (hexane/ethyl acetate = 20/1 (v/v) or pentane/ether = 5/1 (v/v)).

2-(Ferrocenyl-phenyl-methyl)furan (3c).



^{1}H NMR: δ = 7.36 (dd, ^3J = 1.8, ^4J = 0.8, 1 H, 1-H), 7.29-7.18 (m, 5 H, 7-H, 8-H, and 9-H), 6.31 (dd, ^3J = 3.2 Hz, ^3J = 1.8 Hz, 1 H, 2-H), 6.02 (br. d, ^3J = 3.2 Hz, 1H, 3-H), 5.10 (br. s, 1 H, 5-H), 4.21-3.91 (m, 4 H, 11-H and 12-H), 4.03 (s, 5 H, 13-H); ^{13}C NMR: δ = 157.4 (s, C-4), 142.6 (s, C-6), 141.1 (d, C-1), 128.2 (2 × d, C-7 and C-8), 126.6 (d, C-9), 110.0 (d, C-2), 106.4 (d, C-3), 89.9 (s, C-10), 68.8 (d, C-13), 68.8-67.5 (4 × d, C-11 and C-12), 45.6 (d, C-5).

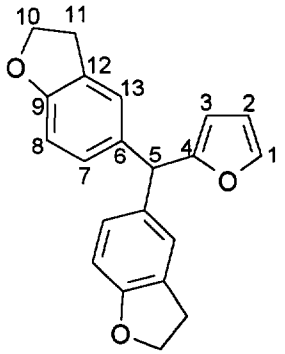
2,5-Bis(ferrocenyl-phenyl-methyl)furan (4c).



1H NMR: δ = 7.31-7.17 (m, 10 H, 5-H, 6-H, and 7-H), 5.96, 5.95 (s, diast. 2 H, 2-H), 5.07, 5.05 (s, diast., 2 H, 3-H), 4.19-3.92 (m, 8 H, 9-H and 10-H), 3.97 (s, 10 H, 11-H); ^{13}C NMR: δ = 156.0 (s, C-1), 143.0, 142.9 (s, diast., C-4), 128.2, 128.1 (2 × d, diast, C-5 and C-6), 126.5, 126.4 (d, diast., C-7), 106.7 (d, C-2), 89.7 (s, C-8), 68.6 (d, C-11), 68.7-67.4 (4 × d, C-9 and C-10), 45.7 (d, C-3). Ratio of diastereomers = 1.5 : 1.

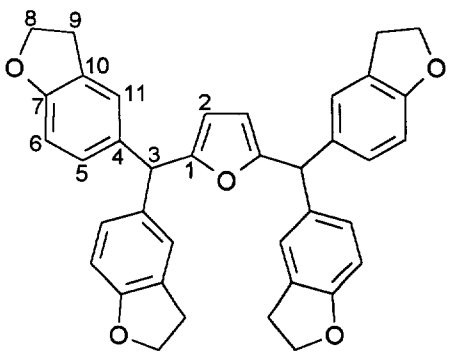
- Reaction of 2c-OMe with 1b. Temperature: 0 °C. Separation and purification of products by column chromatography (hexane/ethyl acetate = 5/1 (v/v)).

2-[Bis(2,3-dihydrobenzo[*b*]furan-5-yl)methyl]furan (3d).



^{1}H NMR: δ = 7.39 (m, 1 H, 1-H), 7.02-7.01 (m, 2 H, 13-H), 6.94-6.92 (m, 2 H, 7-H), 6.73 (d, ^3J = 8.3 Hz, 2 H, 8-H), 6.33-6.32 (m, 1 H, 2-H), 5.93-5.92 (m, 1 H, 3-H), 5.34 (br. s, 1 H, 5-H), 4.56 (t, ^3J = 8.7 Hz, 4 H, 10-H), 3.17 (t, ^3J = 8.7 Hz, 4 H, 11-H); ^{13}C NMR: δ = 158.8 (s, C-9), 157.7 (s, C-4), 141.7 (d, C-1), 134.4 (s, C-6), 128.2 (d, C-7), 127.1 (s, C-12), 125.0 (d, C-13), 110.0 (d, C-2), 108.9 (d, C-8), 107.8 (d, C-3), 71.2 (t, C-10), 49.7 (d, C-5), 29.7 (t, C-11).

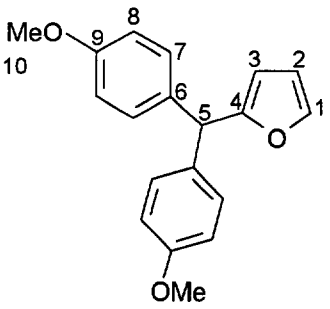
2,5-Bis[bis(2,3-dihydrobenzo[*b*]furan-5-yl)methyl]furan (4d).



^{1}H NMR: δ = 6.96 (m, 4 H, 11-H), 6.90-6.88 (m, 4 H, 5-H), 6.68 (d, ^3J = 8.0 Hz, 4 H, 6-H), 5.79 (s, 2 H, 2-H), 5.26 (s, 2 H, 3-H), 4.53 (t, ^3J = 8.7 Hz, 8 H, 8-H), 3.13 (t, ^3J = 8.7 Hz, 8 H, 9-H); ^{13}C NMR: δ = 158.7 (s, C-7), 156.8 (s, C-1), 134.6 (s, C-4), 128.3 (d, C-5), 126.9 (s, C-10), 125.1 (d, C-11), 108.8 (d, C-6), 108.3 (d, C-2), 71.2 (t, C-8), 49.7 (d, C-3), 29.8 (t, C-9).

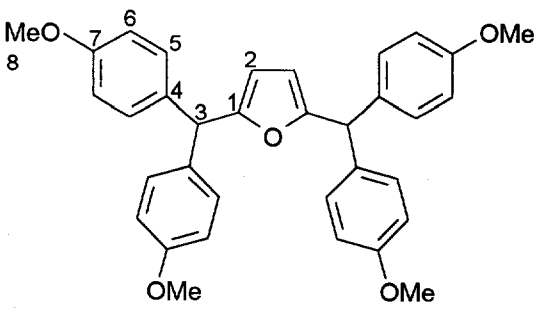
- Reaction of 2d-Cl with 1b. Temperature: 0 °C. Separation and purification by column chromatography (hexane/ethyl acetate = 3/1 (v/v) or pentane/ether = 2/1 (v/v)).

2-[Bis(4-methoxyphenyl)methyl]furan (3e)



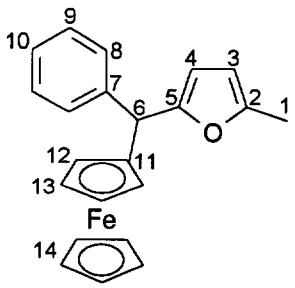
^{1}H NMR: δ = 7.37-7.36 (m, 1 H, 1-H), 7.09-7.04 (AA'BB'-system, J_{AB} = 8.7 Hz, 4 H, 7-H), 6.86-6.78 (AA'BB'-system, J_{AB} = 8.7 Hz, 4 H, 8-H), 6.30-6.29 (m, 1 H, 2-H), 5.89-5.88 (m, 1 H, 3-H), 5.35 (br. s, 1 H, 5-H), 3.78 (s, 6 H, 10-H); ^{13}C NMR: δ = 158.2 (s, C-9) 157.4 (s, C-4), 141.8 (d, C-1), 134.3 (s, C-6), 129.6 (d, C-7), 113.6 (d, C-8), 110.0 (d, C-2), 107.9 (d, C-3), 55.2 (q, C-10), 49.2 (d, C-5).

2,5-Bis[bis(4-methoxyphenyl)methyl]furan (4e).



^{1}H NMR: δ = 7.06-7.03 (AA'BB'-system, J_{AB} = 8.7 Hz, 8 H, 5-H), 6.81-6.77 (AA'BB'-system, J_{AB} = 8.7 Hz, 8 H, 6-H), 5.75 (s, 2 H, 2-H), 5.28 (s, 2 H, 3-H), 3.76 s, 12 H, 8-H); ^{13}C NMR: δ = 158.1 (s, C-7), 156.5 (s, C-1), 134.4 (s, C-4), 129.6 (d, C-5), 113.6 (d, C-6), 108.4 (d, C-2), 55.1 (q, C-8), 49.1 (d, C-3). Colorless needles, mp = 128-130 °C. Anal. Calcd. for $C_{34}H_{32}O_5$ (520.6): C, 78.44; H, 6.20. Found: C, 78.53; H, 6.13.

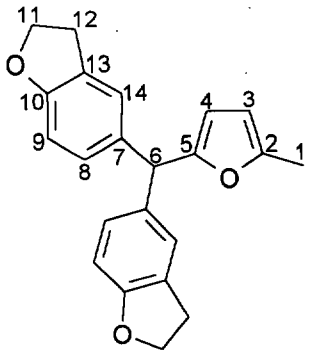
2-(Ferrocenyl-phenyl-methyl)-5-methylfuran (3f).



^{1}H NMR: δ = 7.22-7.12 (m, 5 H, 8-H, 9-H, and 10-H), 5.80-5.79 (m, 1 H, 3-H), 5.76 (br. d, ^3J = 3 Hz, 1 H, 4-H), 4.97 (br. s, 1 H, 6-H), 4.12-3.92 (m, 4 H, 12-H and 13-H), 3.98 (s, 5 H, 14-H), 2.21 (s, 3 H, 1-H); ^{13}C NMR: δ = 155.5 (s, C-5), 150.5 (s, C-2), 142.8 (s, C-7), 128.2 (d, C-9), 128.1 (d, C-8), 126.4 (d, C-10), 107.1 (d, C-4), 105.8 (d, C-3), 90.1 (s, C-11), 68.8 (d, C-14), 68.4-67.4 (4 × d, C-12 and C-13), 45.5 (d, C-6), 13.7 (q, C-1). Temperature: ambient. Purification by column chromatography (hexane/ethyl acetate = 5/1 (v/v)) or

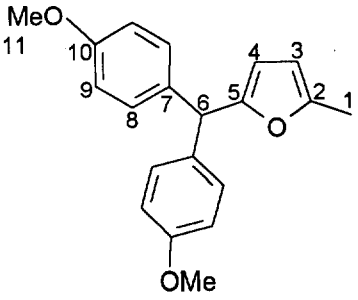
pentane/ether = 5/1 (v/v)) and recrystallization from hexane yields orange oil. Anal. Calcd. for $C_{22}H_{20}OFe$ (356.3): C, 74.14; H, 5.66. Found: C, 73.92; H, 5.78.

2-[Bis(2,3-dihydrobenzo[*b*]furan-5-yl)methyl]-5-methylfuran (3g).



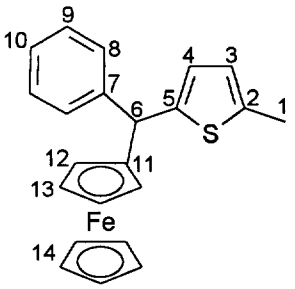
^{1}H NMR: δ = 6.99 (m, 2 H, 14-H), 6.91-6.89 (m, 2 H, 8-H), 6.79 (d, ^3J = 8.3 Hz, 2 H, 9-H), 5.87-5.86 (m, 1 H, 3-H), 5.73 (dd, ^3J = 3.0 Hz, ^4J = 0.4 Hz, 1 H, 4-H), 5.26 (br. s, 1 H, 6-H), 4.54 (t, ^3J = 8.7 Hz, 4 H, 11-H), 3.16 (t, ^3J = 8.7 Hz, 4 H, 12-H), 2.25 (s, 3 H, 1-H); ^{13}C NMR: δ = 158.7 (s, C-10), 155.9 (s, C-5), 151.3 (s, C-2), 134.7 (s, C-7), 128.3 (d, C-8), 127.0 (s, C-13), 125.1 (d, C-14) 108.9 (d, C-9), 108.7 (d, C-4), 105.8 (d, C-3), 71.2 (t, C-11), 49.8 (d, C-6), 29.8 (t, C-12), 13.7 (q, C-1). Temperature: -20 °C. Purification by column chromatography (hexane/ethyl acetate = 4/1 (v/v)) and recrystallization from hexane yields a beige powder with mp = 112-113 °C. Anal. calcd. for $C_{22}H_{20}O_3$ (332.4): C, 79.50; H, 6.06. Found: C, 79.42; H, 6.41.

2-[Bis(4-methoxyphenyl)methyl]-5-methylfuran (3h).



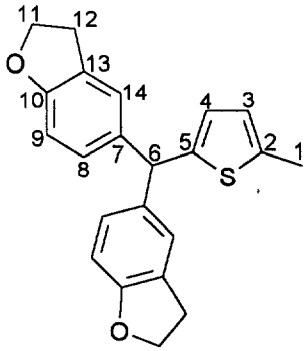
^{1}H NMR: δ = 7.10-7.05 (AA'BB'-system, J_{AB} = 8.7 Hz, 4 H, 8-H), 6.84-6.81 (AA'BB'-system, J_{AB} = 8.7 Hz, 4 H, 9-H), 5.86-5.85 (m, 1 H, 3-H), 5.71 (br. d, ^3J = 2.8 Hz, 1 H, 4-H), 5.29 (br. s, 1 H, 6-H), 3.76 (s, 6 H, 11-H), 2.23 (s, 3 H, 1-H); ^{13}C NMR: δ = 158.2 (s, C-10), 155.5 (s, C-5), 151.3 (s, C-2), 134.5 (s, C-7), 129.6 (d, C-8), 113.7 (d, C-9), 108.7 (d, C-4), 105.8 (d, C-3), 55.2 (q, C-11), 49.2 (d, C-6), 13.6 (q, C-1). Temperature = -70 °C. Purification by column chromatography (hexane/ethyl acetate = 5/1 (v/v)).

2-(Ferrocenyl-phenyl-methyl)-5-methylthiophene (3i).



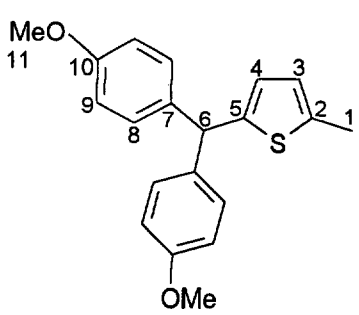
^{1}H NMR: δ = 7.29-7.19 (m, 5 H, 8-H, 9-H, and 10-H), 6.53-6.51 (m, 1 H, 3-H), 6.48 (dd, ^3J = 3.4 Hz, ^4J = 0.7 Hz, 1 H, 4-H), 5.23 (br. s, 1 H, 6-H), 4.20-3.92 (m, 4 H, 12-H and 13-H), 4.02 (s, 5 H, 14-H), 2.40 (br. s, 3 H, 1-H); ^{13}C NMR: δ = 146.4 (s, C-5), 144.8 (s, C-7), 138.2 (s, C-2), 128.3, 128.1 (2 × d, C-8 and C-9) 126.5 (d, C-10), 124.8 (d, C-4), 124.2 (d, C-3), 91.8 (s, C-11), 68.8 (d, C-14), 68.0-67.3 (4 × d, C-12 and C-13), 47.3 (d, C-6), 15.3 (q, C-1). Temperature: ambient. Purification by recrystallization from hexane yields orange oil.

2-[Bis(2,3-dihydrobenzo[*b*]furan-5-yl)methyl]-5-methylthiophene (3k).



^{1}H NMR: δ = 7.08 (m, 2 H, 14-H), 7.01-6.98 (m, 2 H, 8-H), 6.74 (d, ^3J = 8.2 Hz, 2 H, 9-H), 6.60-6.59 (m, 1 H, 3-H), 6.49 (dd, ^3J = 3.4 Hz, ^4J = 0.9 Hz, 1 H, 4-H), 5.50 (br. s, 1 H, 6-H), 4.57 (t, ^3J = 8.7 Hz, 4 H, 11-H), 3.18 (t, ^3J = 8.7 Hz, 4 H, 12-H), 2.45 (s, 3 H, 1-H); ^{13}C NMR: δ = 158.7 (s, C-10), 146.8 (s, C-5), 138.6 (s, C-2), 136.5 (s, C-7), 128.3 (d, C-8), 126.9 (s, C-13), 125.6 (d, C-4), 125.1 (d, C-14), 124.4 (d, C-3), 108.8 (d, C-9), 71.2 (t, C-11), 51.2 (d, C-6), 29.7 (t, C-12), 15.3 (q, C-1). Temperature: ambient. Purification by column chromatography (hexane/ethyl acetate = 20/1 (v/v)) yields yellow oil.

2-[Bis(4-methoxyphenyl)methyl]-5-methylthiophene (3l).



^{1}H NMR: δ = 7.18-7.14 (AA'BB'-system, J_{AB} = 8.7 Hz, 4 H, 8-H), 6.89-6.84 (AA'BB'-system, J_{AB} = 8.7 Hz, 4 H, 9-H), 6.60-6.58 (m, 1 H, 3-H), 6.47 (dd, ^3J = 3.4 Hz, ^4J = 0.9 Hz, 1 H, 4-H), 5.53 (br. s, 1 H, 6-H), 3.81 (s, 6 H, 11-H), 2.44 (s, 3 H, 1-H); ^{13}C NMR: δ = 158.1 (s, C-10), 146.4 (s, C-5), 138.8 (s, C-2), 136.4 (s, C-7), 129.6 (d, C-8), 125.7 (d, C-4), 124.4 (d, C-3), 113.6 (d, C-9), 55.2 (q, C-11), 50.6

(d, C-6), 15.3 (q, C-1). Temperature: -20 °C. Purification by recrystallization from hexane yields colorless needles with mp = 68-69 °C. Anal. calcd. for $C_{20}H_{20}O_2S$ (324.4): C, 74.04; H, 6.21. Found: C, 74.14; H, 6.25.

II. Kinetic Investigations. All reactions were performed in dichloromethane as a solvent.

Kinetic Data for the Reaction of **2a**$^+$OTf with **1a**.

T, °C	$[\mathbf{2c}^+]_0$, mol L^{-1}	$[\mathbf{1a}]_0$, mol L^{-1}	*conversion*, %	*k*, L mol^{-1} s^{-1}
20.0	1.33×10^{-4}	1.36×10^{-3}	57	7.29×10^{-2}
19.8	1.31×10^{-4}	6.72×10^{-3}	54	5.05×10^{-2}
19.9	1.24×10^{-4}	2.78×10^{-3}	63	6.27×10^{-2}
19.9	1.21×10^{-4}	7.21×10^{-3}	53	5.50×10^{-2}

k (20 °C) = $(6.03 \pm 0.85) \times 10^{-2}$ L mol^{-1} s^{-1}

Kinetic Data for the Reaction of **2b**-OAc with **1a**.

T, °C	$[\mathbf{2b}^+]_0$, mol L^{-1}	$[\mathbf{1a}]_0$, mol L^{-1}	$[ZnCl_2 \cdot OEt_2]_0$, mol L^{-1}	*conversion*, %	*k*, L mol^{-1} s^{-1}
-69.2	7.29×10^{-4}	3.63×10^{-3}	7.12×10^{-3}	90	1.15×10^{1}
-59.0	6.09×10^{-4}	2.69×10^{-3}	5.95×10^{-3}	40	3.28×10^{1}
-58.0	6.05×10^{-4}	4.01×10^{-3}	5.91×10^{-3}	92	2.92×10^{1}
-56.1	6.05×10^{-4}	4.01×10^{-3}	5.91×10^{-3}	92	3.50×10^{1}
-48.6	5.38×10^{-4}	2.38×10^{-3}	5.25×10^{-3},[a]	83	5.54×10^{1}
-48.0	7.13×10^{-4}	3.15×10^{-3}	2.32×10^{-3}	83	6.56×10^{1}
-39.3	3.88×10^{-4}	1.93×10^{-3}	5.69×10^{-3}	56	1.06×10^{2}
-29.2	4.97×10^{-4}	2.47×10^{-3}	2.43×10^{-3}	51	1.82×10^{2}

[a] in the presence of 4.0×10^{-3} mol L^{-1} TEBA (Triethylbenzylammonium chloride).

Eyring parameters:

$\Delta H^{\neq} = (26.2 \pm 1.3)$ kJ mol^{-1}

$\Delta S^{\neq} = (-92.2 \pm 5.8)$ J mol^{-1} K^{-1}

k (20 °C) = $(2.00 \pm 0.15) \times 10^{3}$ L mol^{-1} s^{-1}

Kinetic Data for the Reaction of $\mathbf{2b}^+BF_4^-$ with **1b**.

T, °C	$[\mathbf{2b}^+]_0$, mol L^{-1}	$[\mathbf{1b}]_0$, mol L^{-1}	*conversion*, %	*k*, L mol^{-1} s^{-1}
-30.8	1.43×10^{-3}	5.93×10^{-2}	56	3.98×10^{-4}
-11.6	1.42×10^{-3}	2.94×10^{-2}	62	3.15×10^{-3}
10.8	1.39×10^{-3}	5.76×10^{-2}	64	8.42×10^{-3}
20.1	1.39×10^{-3}	5.74×10^{-2}[a]	62	1.82×10^{-2}
20.2	1.62×10^{-3}	6.70×10^{-2}	71	1.99×10^{-2}

[a] in the presence of 2.1×10^{-2} mol L^{-1} TEBA.

Eyring parameters:

$\Delta H^{\neq} = (40.5 \pm 3.4)$ kJ mol^{-1}

$\Delta S^{\neq} = (-139.9 \pm 12.6)$ J mol^{-1} K^{-1}

k (20 °C) $= (1.83 \pm 0.31) \times 10^{-2}$ L mol^{-1} s^{-1}

Kinetic Data for the Reaction of **2c**-OMe with **1b**.

T, °C	$[\mathbf{2c}^+]_0$, mol L^{-1}	$[\mathbf{1b}]_0$, mol L^{-1}	$[TMSOTf]_0$, mol L^{-1}	*conversion*, %	*k*, L mol^{-1} s^{-1}
20.0	1.28×10^{-4}	2.42×10^{-2}	1.95×10^{-3}	71	1.34
20.0	1.27×10^{-4}	6.40×10^{-3}	1.94×10^{-3}	68	1.39
20.0	1.49×10^{-4}	3.75×10^{-3}	2.27×10^{-3}	74	1.24

k (20 °C) $= (1.32 \pm 0.18)$ L mol^{-1} s^{-1}

Kinetic Data for the Reaction of **2d**-Cl with **1b**.

T, °C	$[\mathbf{2c}^+]_0$, mol L^{-1}	$[\mathbf{1b}]_0$, mol L^{-1}	$[TMSOTf]_0$, mol L^{-1}	*conversion*, %	*k*, L mol^{-1} s^{-1}
-70.4	8.60×10^{-5}	1.69×10^{-2}	4.47×10^{-3}	80	7.26×10^{-2}
-61.0	9.49×10^{-5}	1.86×10^{-2}	4.94×10^{-3} [a]	96	1.73×10^{-1}
-50.2	8.64×10^{-5}	8.94×10^{-4}	4.49×10^{-3}	82	7.60×10^{-1}
-40.9	7.57×10^{-5}	7.84×10^{-4}	3.94×10^{-3}	56	1.14
-31.5	7.01×10^{-5}	4.84×10^{-4}	3.65×10^{-3}	92	3.62
-20.0	8.08×10^{-5}	5.57×10^{-4}	2.96×10^{-3} [b]	88	4.16
-20.0	9.09×10^{-5}	1.62×10^{-3}	3.26×10^{-3}	75	4.43

[a] in the presence of 2.4×10^{-3} mol L^{-1} TEBA, [b] with Lewis-Acid $ZnCl_2 \cdot OEt_2$.

Eyring parameters:

$\Delta H^{\neq} = (33.5 \pm 2.6)$ kJ mol^{-1}

$\Delta S^{\neq} = (-97.3 \pm 11.4)$ J mol^{-1} K^{-1}

k (20 °C) $= (5.43 \pm 0.61) \times 10^1$ L mol^{-1} s^{-1}

Kinetic Data for the Reaction of **2b**-OAc with **1c**.

T, °C	$[\mathbf{2c}^+]_0$, mol L^{-1}	$[\mathbf{1c}]_0$, mol L^{-1}	$[TMSOTf]_0$, mol L^{-1}	*conversion*, %	*k*, L mol^{-1} s^{-1}
-69.9	1.78×10^{-3}	3.60×10^{-2}	3.58×10^{-3}	75	0.016
-60.9	1.57×10^{-3}	2.11×10^{-2}	3.15×10^{-3}	80	0.050
-41.4	1.56×10^{-3}	1.61×10^{-2}	1.67×10^{-2}[a]	50	0.198
-40.7	1.72×10^{-3}	1.77×10^{-2}	3.46×10^{-3}	79	0.231
-32.2	1.34×10^{-3}	1.81×10^{-2}	4.49×10^{-3}	60	0.567
-30.9	1.56×10^{-3}	2.10×10^{-2}	1.46×10^{-2}[b]	74	0.591
-30.7	2.08×10^{-3}	2.80×10^{-2}	6.95×10^{-3}	75	0.585

[a] in the presence of 1.3×10^{-2} mol L^{-1} TEBA, [b] in the presence of 1.2×10^{-2} TEBA.

Eyring parameters:

$\Delta H^{\neq} = (34.9 \pm 1.6)$ kJ mol^{-1}

$\Delta S^{\neq} = (-104.1 \pm 6.8)$ J mol^{-1} K^{-1}

k (20 °C) = (13.5 ± 1.8) L mol^{-1} s^{-1}

Kinetic Data for the Reaction of **2c**-OMe with **1c**.

T, °C	$[\mathbf{2c}^+]_0$, mol L^{-1}	$[\mathbf{1c}]_0$, mol L^{-1}	$[TMSOTf]_0$, mol L^{-1}	*conversion*, %	*k*, L mol^{-1} s^{-1}
-66.3	1.68×10^{-4}	4.31×10^{-3}	1.40×10^{-2}[a]	91	5.01
-65.1	7.59×10^{-4}	9.73×10^{-3}	5.07×10^{-3}	58	4.83
-63.5	7.67×10^{-4}	9.82×10^{-3}	5.12×10^{-3}	95	5.20
-56.4	5.67×10^{-4}	1.16×10^{-2}	3.78×10^{-3}	93	9.05
-53.8	8.43×10^{-4}	1.08×10^{-2}	5.63×10^{-3}	82	9.26
-45.7	7.75×10^{-4}	7.94×10^{-3}	5.17×10^{-3}	89	15.54
-35.7	6.37×10^{-4}	6.53×10^{-3}	4.25×10^{-3}	87	26.64

[a] in the presence of 1.1×10^{-2} mol L^{-1} TEBA

Eyring parameters:

$\Delta H^{\neq} = (21.3 \pm 0.9)$ kJ mol^{-1}

$\Delta S^{\neq} = (-126.1 \pm 4.4)$ J mol^{-1} K^{-1}

k(20 °C) = $(2.53 \pm 0.14) \times 10^2$ L mol^{-1} s^{-1}

Kinetic Data for the Reaction of **2b**-OAc with **1d**.

T, °C	$[\mathbf{2b}^+]_0$, mol L^{-1}	$[\mathbf{1d}]_0$, mol L^{-1}	$[TMSOTf]_0$, mol L^{-1}	*conversion*, %	*k*, L mol^{-1} s^{-1}
19.6	2.27×10^{-3}	4.18×10^{-2}	5.57×10^{-3}	52	6.29×10^{-2}
19.7	2.36×10^{-3}	8.68×10^{-2}	4.63×10^{-3}	56	6.70×10^{-2}
19.7	2.00×10^{-3}	7.35×10^{-2}	$2.06 \times 10^{-2,a}$	70	6.54×10^{-2}

[a] in the presence of 1.7×10^{-2} mol L^{-1} TEBA

k (20 °C) = $(6.51 \pm 0.17) \times 10^{-2}$ L mol^{-1} s^{-1}

Kinetic Data for the Reaction of **2c**-OMe with **1d**.

T, °C	$[\mathbf{2c}^+]_0$, mol L^{-1}	$[\mathbf{1d}]_0$, mol L^{-1}	$[TMSOTf]_0$, mol L^{-1}	*conversion*, %	*k*, L mol^{-1} s^{-1}
-20.0	1.36×10^{-4}	2.31×10^{-3}	3.12×10^{-3}	66	2.53×10^{-2}
0.0	1.38×10^{-4}	8.16×10^{-3}	3.15×10^{-3}	69	1.12×10^{-1}
10.0	1.40×10^{-4}	1.24×10^{-2}	4.27×10^{-3}	80	2.60×10^{-1}
20.0	1.15×10^{-4}	1.71×10^{-3}	3.52×10^{-3}	64	4.35×10^{-1}
20.0	1.22×10^{-4}	5.45×10^{-3}	1.87×10^{-3}	64	4.80×10^{-1}

Eyring parameters:

$\Delta H^{\neq}$ = (42.7 ± 1.3) kJ mol^{-1}

$\Delta S^{\neq}$ = (-105.6 ± 4.8) J mol^{-1} K^{-1}

k (20 °C) = (0.46 ± 0.08) L mol^{-1} s^{-1}

Kinetic Data for the Reaction Of **2d**-Cl with **1d**.

T, °C	[**2d**$^+$], mol L^{-1}	[**1d**], mol L^{-1}	[TMSOTf], mol L^{-1}	conversion, %	k, L mol^{-1} s^{-1}
-70.0	1.05×10^{-4}	1.14×10^{-3}	4.10×10^{-3}	46	3.41×10^{-2}
-60.4	9.46×10^{-5}	9.23×10^{-3}	3.69×10^{-3}	68	8.22×10^{-2}
-50.3	8.47×10^{-5}	1.83×10^{-3}	3.30×10^{-3}	50	1.96×10^{-1}
-40.5	9.78×10^{-5}	9.54×10^{-3}	3.81×10^{-3}	92	4.04×10^{-1}
-31.7	7.77×10^{-5}	1.68×10^{-3}	6.06×10^{-2}[a]	53	1.11
20.0	7.51×10^{-5}	7.12×10^{-4}	2.69×10^{-3}	93	2.16×10^{1}

[a] in the presence of 2.12×10^{-2} mol L^{-1} TEBA

Eyring parameters:

$\Delta H^{\neq} = (33.9 \pm 0.9)$ kJ mol^{-1}

$\Delta S^{\neq} = (-103.7 \pm 3.9)$ J mol^{-1} K^{-1}

k (20°C) $= (2.13 \pm 0.19) \times 10^{1}$ L mol^{-1} s^{-1}